

Organic Derivatives of Arsenic, Antimony and Bismuth

Part I. Distibyls.—Tetraphenyldistibyl. Attempts to Obtain
Tetraphenyldibismuthyl. Tetra-*p*-Bromotetraphenyl- and
Tetra-*p*-Tolyldistibyl. Di-Alpha-Naphthyl iodostibine

Part II. The Interaction of Diarylarsyl Iodides, Diarylstibyl
Iodides and Phenyl dihaloarsines with the Piperidine Salt
of N-Pentamethylenedithiocarbamic Acid

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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UNIVERSITY OF MICHIGAN

By
U. O. Oakdale
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PART I

DISTIBYLS. I. TETRAPHENYLDISTIBYL. ATTEMPTS TO OBTAIN TETRAPHENYLDIBISMUTHYL.¹ TETRA-*p*- BROMOTETRAPHENYL- AND TETRA-*p*-TOLYLDISTIBYL. DI- α -NAPHTHYLIODOSTIBINE

We began our present study in the hope that we might obtain tetraphenyldistibyl, $(\text{C}_6\text{H}_5)_2\text{Sb}-\text{Sb}(\text{C}_6\text{H}_5)_2$, and tetraphenyldibismuthyl, $(\text{C}_6\text{H}_5)_2\text{Bi}-\text{Bi}(\text{C}_6\text{H}_5)_2$, compounds analogous to the diarsyls² which have been investigated recently in this Laboratory. It was found that the first mentioned compound could be prepared from the interaction of diphenylstibyl iodide and sodium hypophosphite.³

Tetraphenyldistibyl, in solution, proved to be extremely reactive toward oxygen and the gas was absorbed with the same rapidity which is so characteristic of a solution of a tetra-aryldiarsyl or a triarylmethyl; hence the preparation of the distibyl was carried out in a free radical apparatus and the product isolated in an atmosphere of nitrogen or carbon dioxide. The amount of oxygen absorbed corresponded to that required for the formation of tetraphenylstibyl peroxide, $(\text{C}_6\text{H}_5)_2\text{Sb}-\text{O}-\text{O}-\text{Sb}(\text{C}_6\text{H}_5)_2$. The

¹ This investigation was made possible by the aid of the Parke, Davis and Company Fellowship and by a grant from the Faculty Research Fund of the University of Michigan.

² Blicke and Smith, *J. Am. Chem. Soc.*, **51**, 2272 (1929); Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 780 (1930); Blicke and Smith, *ibid.*, **52**, 2937 (1930).

³ Schmidt [*Ann.*, **421**, 235 (1920)] stated that tetraphenylstibyl oxide, $(\text{C}_6\text{H}_5)_2\text{Sb}-\text{O}-\text{Sb}(\text{C}_6\text{H}_5)_2$, when treated with hypophosphorous acid, yields a yellow compound which he thought might be tetraphenyldistibyl. However, no analysis or further description of the material was recorded.

colorless, crystalline distibyl possessed a sharp melting point and dissolved in organic solvents with the formation of colorless solutions.

Diphenylbismuthyl iodide, dissolved in bromobenzene, was shaken with molecular silver, mercury, zinc powder and copper bronze, respectively. In the case of the first two metals black precipitates were formed. However, none of the solutions obtained absorbed oxygen. Sodium hypophosphite, at ordinary temperature, did not seem to react with an alcoholic solution of diphenylbismuthyl iodide. When the mixture was warmed a black product was produced. A mixture of diphenylbismuthyl iodide, bromobenzene and copper was placed in an absorption flask, connected with an oxygen reservoir, and shaken vigorously for eight hours. The absorption of oxygen, based on peroxide formation, was approximately 50% of the calculated amount. Similar results were obtained with molecular silver.

It has been shown that tetraphenyldistibyl⁴ behaves similarly to tetraaryldiarsyls in that it reacts almost instantly with an amount of oxygen equivalent to that required for the formation of a peroxide. An analogous behavior characterizes the new distibyls which we have prepared—tetra-*p*-bromotetraphenyl- and tetra-*p*-tolyl-distibyl.

No evidence could be obtained by molecular weight determinations in favor of the assumption that tetraphenyl- or tetra-*p*-tolyl-distibyl dissociates into diarylstibyl radicals.⁵

In the case of di- α -naphthylidostibine only a few grams of the pure iodide were isolated by a laborious process from five kilograms of α -naphthylamine, hence the corresponding distibyl was not prepared.

The diarylidostibines, which yielded the distibyls when treated with sodium hypophosphite, were synthesized by means of the following series of reactions: the required aryl amine was diazotized and allowed to react with antimony trichloride, the arylstibinic acid produced was reduced to the aryl-dichlorostibine and the latter hydrolyzed to the corresponding oxide. The oxide, when heated, was converted into the tetraarylstibyl oxide and antimony trioxide.⁶ Treatment with acetic acid converted the tetraarylstibyl oxide into the diarylstibyl acetate; this compound yielded the diarylidostibine when mixed with hydriodic acid.

Experimental Part

Diphenylstibyl Iodide.—Two hundred grams of crude, dry phenylstibinic acid⁷ was dissolved in 500 cc. of hydrochloric acid and 250 cc. of water added to precipitate colored

(4) Blicke and Oakdale, *J. Am. Chem. Soc.*, **53**, 1025 (1931).

(5) Failure to obtain data indicative of dissociation by molecular weight determinations does not prove that distibyls do not dissociate in solution; the degree of dissociation may be of such a low magnitude that it cannot be detected by the ordinary molecular weight procedures.

(6) This series of reactions was developed for the preparation of organic antimony compounds by Schmidt, *Ann.*, **421**, 234 (1920).

⁷ Schmidt, *Ann.*, **421**, 189 (1920).

impurities. After filtration the solution of phenylstibinic acid was cooled with ice and treated with sulfur dioxide for three hours. The mixture was then allowed to remain in an ice-bath for six hours. The phenyldichlorostibine,⁸ which had separated in crystalline form, was filtered with suction. To prepare phenylstibine oxide a cold acetone solution of phenyldichlorostibine was added, dropwise, to cold dilute ammonia water. The mixture was stirred vigorously during this process and kept cold by the addition of ice. The precipitated phenylstibine oxide was filtered with suction, washed with acetone and dried.

Twenty-gram portions of finely powdered, crude phenylstibine oxide were placed in 250-cc. Erlenmeyer flasks fitted with two-holed stoppers through which inlet and outlet tubes were inserted. A stream of dry nitrogen was passed through the flasks and the latter were heated at 90° in an oil-bath for two hours. The viscous reaction products, which contained tetraphenylstibyl oxide, were extracted several times with hot alcohol, the alcoholic extracts filtered and the alcohol removed.⁹ The oily residue obtained from each twenty-gram portion of phenylstibine oxide was treated with 10 cc. of acetic acid and stirred, whereupon the material crystallized almost immediately. This substance, diphenylstibyl acetate, was filtered with suction and recrystallized from acetic acid; 1 cc. of acetic acid was used for each gram of the acetate; m. p. 133–135°.¹⁰

In order to convert the acetate into the corresponding chloride or bromide, or the chloride into the iodide, it is essential that all products should be in a very pure state before the conversion is attempted.

For the preparation of diphenylstibyl chloride 20 g. of pure diphenylstibyl acetate was dissolved in 60 cc. of hot acetic acid. The solution was cooled quickly to room temperature and 80 cc. of hydrochloric acid was added immediately in small portions. The mixture was cooled during the addition of the hydrochloric acid. The chloride precipitated at once in crystalline form and was recrystallized from an equal weight of acetic acid; m. p. 68°.¹¹

When diphenylstibyl acetate was dissolved in hot acetic acid, the solution cooled to room temperature and an excess of 48% hydrobromic acid added an oil precipitated. When cooled the latter became solid. After three recrystallizations from acetic acid the compound, undoubtedly diphenylstibyl bromide, melted at 86°.

Diphenylstibyl iodide was prepared as follows. Twenty grams of the chloride, dissolved in 25 cc. of pure acetone, was added to three times the calculated amount of sodium iodide dissolved in the same solvent. After twelve hours the sodium chloride was removed and the acetone allowed to evaporate spontaneously. The crystalline iodide, obtained after the addition of water to the residue, was recrystallized twice from acetic acid and twice from absolute alcohol; m. p. 68–70°. The iodide is not affected by cold water and is hydrolyzed only very slowly by boiling water.

*Anal.*¹² Calcd. for $C_{12}H_{10}SbI$: Sb, 30.23; I, 31.51. Found: Sb, 30.20; I, 31.42.

Neither diphenylstibyl iodide nor triphenylmethyl bromide, dissolved in bromobenzene, absorbs oxygen. When diphenylstibyl iodide (0.003 mole) and triphenylmethyl bromide (0.003 mole) were put into a test-tube, the latter constricted and then filled quickly with bromobenzene which had been saturated with nitrogen a deep red solution was formed immediately. When the tube was broken in an oxygen absorption appa-

⁸ Solutions of this material are powerful skin irritants.

⁹ This process represents a slight modification of that used by Schmidt [*Ann.*, **421**, 234 (1920)] for the conversion of phenylstibine oxide into tetraphenylstibyl oxide

¹⁰ Schmidt [*Ann.*, **429**, 140 (1922)] recorded the melting point as 132°.

¹¹ Michaelis and Günther, *Ber.*, **44**, 2318 (1911).

¹² Method of Thompson and Oakdale, *J. Am. Chem. Soc.*, **52**, 1195 (1930).

ratus¹³ 51 cc. of oxygen was absorbed very rapidly. This quantity of oxygen is more than that required for the formation of triphenylmethyl peroxide (34.2 cc.) and is less than that necessary for the formation of both triphenylmethyl peroxide and tetraphenylstibyl peroxide. A phenomenon entirely analogous to that described above is observed when diphenylarsyl iodide and triphenylmethyl bromide are mixed.¹⁴

Action of Metals on Diphenylstibyl Iodide.—Two tubes were prepared each of which contained diphenylstibyl iodide, bromobenzene¹⁵ and copper bronze.¹⁶ After the tubes had been shaken for a definite period of time the one tube was broken in an oxygen absorption apparatus while the contents of the other tube were analyzed for copper halide. Several series of such tubes were shaken for different periods of time. The data obtained showed that the percentage of iodine removed, which should serve as a measure of the amount of tetraphenylstibyl formed, did not correspond to the percentage of oxygen absorbed. The latter was calculated based on the assumption that tetraphenylstibyl peroxide, $(C_6H_5)_2Sb-O-O-Sb(C_6H_5)_2$, is the primary product of the oxidation. These results indicate that the distibyl undergoes decomposition or that it is rendered inactive toward oxygen by combination with unchanged diphenylstibyl iodide or the copper halide. However, we have shown that the isolated distibyl, dissolved in bromobenzene, retains its activity toward oxygen for a period of several days at least.

In one instance the distibyl was allowed to absorb oxygen as fast as it was formed. One and six-tenths grams of diphenylstibyl iodide, 15 cc. of bromobenzene and 2 g. of copper were placed in an absorption flask attached to a reservoir filled with oxygen and the absorption flask was shaken vigorously and continuously. After five minutes 20 cc., after one hour 32 cc. and after nine hours 44.8 cc., the amount of the gas calculated for peroxide formation, had been absorbed. An analysis of the copper halide formed showed that practically all of the iodine had been removed from the diphenylstibyl iodide at the end of nine hours.

Tetraphenylstibyl.—Three and two-tenths grams of diphenylstibyl iodide, dissolved in 25 cc. of absolute alcohol, was poured into a free radical apparatus¹⁷ of 125-cc. capacity. One and three-tenths grams of sodium hypophosphite was dissolved in 5 cc. of water and 20 cc. of alcohol added. This solution was then poured into the radical apparatus. The reaction mixture was protected from light and allowed to remain at ordinary temperature for twelve hours. The distibyl separated from the mixture in the form of pale yellow-green needles. The liquid was decanted through the stopcock with the aid of suction and the product was washed several times with small amounts of alcohol, whereupon it became practically colorless. The compound was dried by allowing the apparatus to remain attached to the suction pump for six hours. The material was then removed from the radical apparatus in the manner described previously in the case of diarsyls.¹⁸ The amount of distibyl isolated was usually somewhat in excess of one gram.

The product when pure was practically colorless and the copper wire test proved it to be halogen free. In a sealed tube filled with nitrogen it melted at 121–122°. In order to prevent oxidation during the weighing of the material it was found advantageous

¹³ Gomberg and Schoepfle, *ibid.*, **39**, 1661 (1917).

¹⁴ Blicke and Smith, *ibid.*, **51**, 2275 (1929).

¹⁵ This solvent was used because of its comparatively low vapor pressure. Gomberg and Schoepfle, *ibid.*, **39**, 1661 (1917).

¹⁶ Magnesium powder, molecular silver, mercury and zinc dust were tried but only copper and zinc seemed to remove the halogen rapidly.

¹⁷ Gomberg and Schoepfle, *J. Am. Chem. Soc.*, **39**, 1659 (1917). The lower stopcock on the apparatus was removed.

¹⁸ Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 782 (1930).

to compress the distibyl in the form of tablets in a tablet machine. Each tablet was then weighed in a closed tube, filled with nitrogen, just large enough to contain it.

*Anal.*¹² Calcd. for $C_{24}H_{20}Sb_2$: Sb, 43.93. Found: Sb, 44.13.

The diarsyl reacts instantly with iodine. In an apparatus filled with nitrogen there was placed 0.4320 g. of the distibyl. The latter was then dissolved in 15 cc. of benzene and a *N*/10 solution of iodine in carbon tetrachloride was added. The iodine color disappeared instantly but after 15.8 cc. of the solution had been added a permanent color was produced. The calculated amount of iodine solution necessary for the formation of diphenylstibyl iodide is 15.7 cc. The solution was poured into a dish and the carbon tetrachloride evaporated. The yellow, crystalline residue was washed with a very small amount of acetic acid; m. p. 64–65°. Mixed with diphenylstibyl iodide it melted at the same temperature.

Potassium permanganate, dissolved in acetone, is decolorized instantly by the distibyl.

A portion of the isolated tetraphenyldistibyl, which weighed 0.7609 g., was dissolved in bromobenzene and the solution preserved in a sealed tube, protected from light for four days. The tube was then broken in an oxygen absorption apparatus. Twenty-nine cc. of oxygen was absorbed almost instantly; the calculated amount is 29.4 cc.

Triphenylbismuthine.—Phenylmagnesium bromide was prepared from 80 g. of bromobenzene (0.5 mole), 12 g. of magnesium and 300 cc. of ether. After the addition of 200 cc. of dry benzene the solution was stirred vigorously and 41 g. of finely-divided, freshly distilled bismuth trichloride (0.13 mole)¹⁹ was added in five portions during the course of one-half hour. The mixture was then heated on a steam-bath and stirred for four hours. The mixture was decomposed with ice and ammonium chloride, the ether layer separated and dried with fused sodium sulfate. After removal of the solvent the oily residue soon solidified. The material was washed with petroleum ether (30–60°); m. p. 76–77°; yield, 48 g., or 84% of the calculated amount.²⁰

Diphenylbismuthyl Iodide.—Twenty-three grams of diphenylbismuthyl chloride²¹ was dissolved in 200 cc. of absolute alcohol, 9 g. of solid sodium iodide added and the mixture shaken for twelve hours. It was then poured into 600 cc. of boiling water. Diphenylbismuthyl iodide separated in the form of yellow flakes. The latter were filtered, washed with water and dried in a vacuum desiccator. The product was treated with hot ethyl acetate in order to dissolve the diphenylbismuthyl iodide, the mixture cooled to room temperature and filtered to remove the red by-product. The solvent was distilled from the filtrate under diminished pressure in a stream of nitrogen. The iodide was powdered, triturated with 20 cc. of petroleum ether (30–60°) in order to remove triphenylbismuthine, the petroleum ether decanted and the process repeated several times; m. p. 132–134°.²²

Diphenylbismuthyl iodide, dissolved in acetone, instantly decolorizes potassium permanganate dissolved in the same solvent. If a carbon tetrachloride solution of iodine is added to the bismuthyl iodide, dissolved in benzene, the first portion of the iodine

¹⁹ The best quality of bismuth trichloride which we could obtain contained considerable liquid. The material was drained thoroughly, placed on a porous plate and the latter put into a desiccator. After several days the chloride was distilled from a retort with a very short side arm.

²⁰ From phenylmagnesium bromide and bismuth trichloride Pfeiffer [*Ber.*, **37**, 4622 (1904)] obtained a 25% yield of triphenylbismuthine.

²¹ Challenger and Allpress, *J. Chem. Soc.*, **107**, 19 (1915).

²² Gillmeister [*Ber.*, **30**, 2843 (1897)] obtained the iodide from triphenylbismuthine dichloride and sodium iodide.

solution is decolorized immediately. Upon further addition of iodine a brick-red and then a brown precipitate is formed.

***p*-Bromophenyldichlorostibine.**—*p*-Bromophenylstibinic acid²³ was obtained from *p*-bromoaniline according to the method used by Dunning and Reid²⁴ for the preparation of other arylstibinic acids. Two hundred grams of the air-dried acid was dissolved in 500 cc. of cold, concd. hydrochloric acid, the solution stirred and 550 cc. of water added. The flocculent material was removed by filtration and 25 g. of charcoal was added to the red filtrate, the mixture shaken frequently and filtered after twelve hours. The filtrate was cooled with ice and saturated with sulfur dioxide. The *p*-bromophenyldichlorostibine (40–60 g.) which precipitated was air dried and recrystallized from heptane; m. p. 90–92°. The dichloro compound is very soluble in benzene, less soluble in acetic acid.

Anal. Calcd. for $C_6H_4SbCl_2Br$: Sb, 34.93; Cl, 20.34; Br, 22.92. Found: Sb, 34.77; Cl, 20.22; Br, 23.10.

***p*-Bromophenyldiiodostibine.**—In order to obtain *p*-bromophenylstibine oxide, 35 g. of the dichloride was dissolved in 100 cc. of acetone and added slowly to a mixture prepared from 1000 cc. of water, 100 cc. of ammonia water and ice. The oxide which precipitated was filtered and air dried. To a solution of 12.5 g. of the oxide in 30 cc. of acetic acid, 14 cc. of hydriodic acid (sp. gr. 1.65) was added; *p*-bromophenyldiiodostibine precipitated as a yellow, crystalline solid. The material was washed thoroughly with water and dried in a desiccator; yield 22 g. The iodide was recrystallized from absolute alcohol which contained a small amount of hydriodic acid; m. p. 124–125°.

Anal. Calcd. for $C_6H_4SbBrI_2$: Br, 15.03; I, 47.76. Found: Br, 15.25; I, 47.69.

Di-*p*-bromodiphenyliodostibine.—Di-*p*-bromodiphenylstibyl acetate was obtained in the following manner: 20 g. of *p*-bromophenylstibine oxide was placed in an Erlenmeyer flask and heated in a bath (145°) in a stream of nitrogen for one hour. The pasty material was extracted with hot alcohol, the alcoholic solution filtered and the solvent removed. The oily tetra-*p*-bromotetraphenylstibyl oxide was treated with a small amount of acetic acid, whereupon it became crystalline through conversion of the stibyl oxide into the corresponding acetate; the yield of crude product was 17 g. In order to recrystallize the acetate, 10 g. of the material was dissolved in a mixture of 5 cc. of acetic acid, 10 cc. of benzene and 40 cc. of heptane. The acetate melts at 134–135°.

To 4.9 g. of the acetate, dissolved in 20 cc. of hot acetic acid, there was added 2 cc. of hydriodic acid (sp. gr. 1.65). The mixture was cooled with ice and the crystalline di-*p*-bromodiphenyliodostibine removed by filtration. The iodide was thoroughly dried and then extracted in a Soxhlet apparatus with 150 cc. of petroleum ether (30–60°). The petroleum ether solution was decanted from the oily impurity which adhered to the sides of the extraction flask. The iodide, which separated from the cold solution, was recrystallized from heptane; m. p. 73–74°. The material is quite soluble in alcohol and benzene.

Anal. Calcd. for $C_{12}H_8SbBr_2I$: Sb, 21.72; Br, 28.51; I, 22.64. Found: Sb, 21.60; Br, 28.76; I, 22.64.

Tetra-*p*-bromotetraphenyldistibyl.—A solution of 4 g. of di-*p*-bromodiphenyliodostibine in 50 cc. of absolute alcohol and 2.5 g. of sodium hypophosphite, dissolved in 4 cc. of water and 4 cc. of alcohol, was poured into a free-radical bulb and after twelve hours the liquid decanted from the tan colored, crystalline precipitate. The product was washed twice with a mixture of 25 cc. of alcohol and 2 cc. of water, twice with absolute alcohol, twice with 20 cc. of hot xylene and finally with petroleum ether (30–60°). The product was dried under diminished pressure in a bath at 60° and isolated in a car-

(23) Fargher and Gray, *J. Pharmacol.*, **18**, 354 (1921).

(24) All stibinic acids were prepared according to the general method of Dunning and Reid, *J. Am. Chem. Soc.*, **49**, 2871 (1927).

bon dioxide atmosphere. The light greenish-yellow distibyl melted with decomposition at 211–213° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{24}H_{16}Sb_2Br_4$: Sb, 28.08; Br, 36.85. Found: Sb, 27.95; Br, 36.83.

Dissolved in bromobenzene 1.272 g. of the distibyl absorbed 34 cc. (N. T. P.) of oxygen in one minute; calcd. absorption, 33 cc.

Di-*p*-tolyliodostibine.—To 400 g. of crude *p*-tolylstibinic acid, dissolved in 800 cc. of warm concd. hydrochloric acid, 800 cc. of water was added and the cold mixture filtered. The filtrate was diluted further with water until it became turbid. Sulfur dioxide was passed into the solution for a few minutes and after the removal of the gum the filtrate was cooled with ice and saturated with sulfur dioxide; yield 150 g. of practically colorless, crystalline *p*-tolyldichlorostibine; m. p. 89–92°. ²⁶

The dichlorostibine was dissolved in acetone and treated with ammonia water, whereupon *p*-tolylstibine oxide was obtained. The latter was washed with acetone and dried. *p*-Tolylstibine oxide was heated in a bath (100°) for two hours in order to convert it into tetra-*p*-tolylstibyl oxide. The crude oxide was extracted with hot alcohol. After recrystallization from alcohol the oxide melted at 101°.

Anal. Calcd. for $C_{28}H_{28}OSb_2$: Sb, 38.57. Found: Sb, 39.04.

In order to obtain di-*p*-tolylstibyl acetate, tetra-*p*-tolylstibyl oxide was dissolved in hot acetic acid. The acetate separated in crystalline form when the solution cooled; after recrystallization from heptane the acetate melted at 122–123°.

Anal. Calcd. for $C_{16}H_{17}O_2Sb$: Sb, 33.55. Found: Sb, 33.07.

To 10 g. of di-*p*-tolylstibyl acetate, dissolved in 50 cc. of acetic acid, 20 cc. of constant boiling hydriodic acid, diluted with 20 cc. of water, was added. The crude di-*p*-tolyliodostibine was washed free from hydriodic acid and extracted with petroleum ether; m. p. after recrystallization from absolute alcohol, 76–78°. ²⁶

Anal. Calcd. for $C_{14}H_{14}SbI$: Sb, 28.26; I, 29.46. Found: Sb, 28.23; I, 29.30.

Tetra-*p*-tolyldistibyl.—A solution, prepared from 3.5 g. of di-*p*-tolyliodostibine and 60 cc. of absolute alcohol, was poured into a free radical apparatus. There was added 2.5 g. of sodium hypophosphite, dissolved in 5 cc. of water and 20 cc. of alcohol. After twelve hours the supernatant liquid was decanted from the pale greenish-yellow crystals, the material washed several times with 90% alcohol and then with absolute alcohol. The product was isolated in a carbon dioxide atmosphere; m. p. 155–157° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{28}H_{28}Sb_2$: Sb, 40.07. Found: Sb, 39.50.

Dissolved in bromobenzene 0.917 g. of the distibyl absorbed 40 cc. (N. T. P.) of oxygen in three minutes; calcd. absorption 34 cc.

TABLE I
MOLECULAR WEIGHT DETERMINATIONS

The determinations were made in benzene by the Menzies method. A current of dry nitrogen was passed over the top of the apparatus during the determinations

Concn., %	ΔT , °C.	Mol. wt. found	Mol. wt. calcd. for $R_2Sb-SbR_2$
1.48	0.0766	621	607
2.44	.1250	627	
3.29	.1744	607	
4.32	.2248	619	

(25) Hasenbäumer, *Ber.*, **31**, 2914 (1898).

(26) Goddard and Yarsley [*J. Chem. Soc.*, 719 (1928)] described a compound, m. p. 233°, as di-*p*-tolyliodostibine which they obtained from tri-*p*-tolylstibine di-iodide. The high melting point alone indicates that their substance must possess a different structure.

Di- α -naphthylodostibine.—Two hundred grams of crude, dry α -naphthylstibinic acid²⁷ was dissolved in 500 cc. of cold hydrochloric acid, 200 cc. of water added and the mixture stirred for some time. After the removal of a black by-product by filtration, the filtrate was shaken with 25 g. of charcoal for twelve hours, filtered and the filtrate centrifuged in order to separate a black oil. The clear filtrate was cooled with ice and saturated with sulfur dioxide; α -naphthylchlorostibine separated in crystalline form. After recrystallization from heptane, the material melted at 105–106°. The chloride is very soluble in benzene and absolute alcohol.

Anal. Calcd. for $C_{12}H_7SbCl_2$: Sb, 38.08; Cl, 22.18. Found: Sb, 38.07; Cl, 21.95.

The dichlorostibine was hydrolyzed in the manner described above and 25 g. of the crude α -naphthylstibine oxide was heated (bath temperature 105–110°) in a stream of nitrogen for forty-five minutes. The tetra- α -naphthylstibyl oxide formed was extracted from the pasty reaction mixture with acetone and the acetone removed. The oxide was dissolved in 35 cc. of acetic acid and 8 cc. of constant boiling hydriodic acid was added. Yellow di- α -naphthylodostibine separated as an oil which became crystalline when cooled and rubbed. The dry iodide was extracted with petroleum ether; m. p. 136–137°.

Anal. Calcd. for $C_{20}H_{14}SbI$: Sb, 24.22; I, 25.24. Found: Sb, 24.19; I, 25.22.

Procedure for the Determination of Antimony.—Compounds in which both antimony and halogen were to be determined were analyzed by the method of Thompson and Oakdale.²⁸ However, if antimony only is to be estimated, decomposition of the organic material can be effected in five minutes according to the following procedure. The sample and 20 cc. of concd. sulfuric acid are boiled in a 300-cc. Kjeldahl flask. If the sample contains iodine, the latter must be removed at this stage by the addition of several 2-cc. portions of hydrogen peroxide. Perchloric acid (70%) is added, dropwise, until the solution becomes colorless; 1 cc. is usually sufficient. The mixture is boiled for five minutes longer, cooled and diluted with four times its own volume of water. The pentavalent antimony is reduced to the trivalent state by treatment of the solution with sulfur dioxide for a short time. After the solution has been heated on a water-bath for one hour, it is boiled for fifteen minutes to remove sulfur dioxide completely, transferred to a 500-cc. Erlenmeyer flask and 10 cc. of concd. hydrochloric acid added. It is then titrated, at 60°, with 0.1 *N* potassium bromate solution with the use of methyl orange as indicator.

Summary

Tetraphenyldistibyl, $(C_6H_5)_2Sb-Sb(C_6H_5)_2$, has been prepared from diphenylstibyl iodide and sodium hypophosphite. The distibyl, in solution, is just as reactive toward oxygen as solutions of tetra-aryldiarsyls or triarylmethyls.

We have not been able to obtain tetraphenyldibismuthyl by the methods used for the preparation of the analogous arsenic and antimony compounds.

The following antimony compounds, hitherto unknown, have been prepared in a pure state: *p*-bromophenyldichlorostibine, *p*-bromophenyldiodostibine, di-*p*-bromodiphenylstibyl acetate, di-*p*-bromodiphenyliodo-

(27) Riddell and Basterfield, *Trans. Royal Soc. Canada*, Third Series, Vol. XXIII, Part 1, Section III, p. 48 (1929).

(28) Thompson and Oakdale, *J. Am. Chem. Soc.*, **52**, 1199 (1930).

stibine, tetra-*p*-bromotetraphenyldistibyl, tetra-*p*-tolylstibyl oxide, di-*p*-tolylstibyl acetate, di-*p*-tolylstibyl iodide, tetra-*p*-tolylstibyl, α -naphthylchlorostibine and di- α -naphthylstibine.

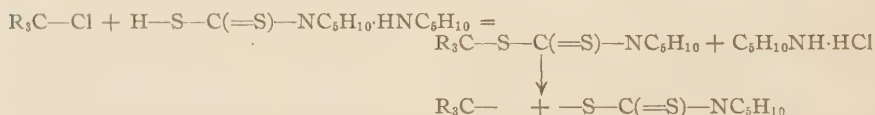
The distibyls possess properties similar to those of diarsyls.

A procedure for the determination of antimony is described.

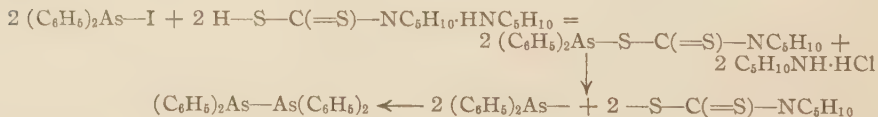
PART II

THE INTERACTION OF DIARYLARSYL IODIDES, DIARYLSTIBYL
IODIDES AND PHENYLDIHALOARSINES WITH THE
PIPERIDINE SALT OF N-PENTAMETHYLENE-
DITHIOCARBAMIC ACID

N-Pentamethylene-S-triarylmethyldithiourethans are formed almost instantly and quantitatively from the interaction, at ordinary temperature, of a triarylmethyl halide and the piperidine salt of N-pentamethylenedithiocarbamic acid. These urethans are of interest because of the fact that they dissociate spontaneously, in solution, with the formation of triarylmethyls.¹



In view of the great reactivity of the halogen in diarylarsyl and diarylstibyl iodides it seemed probable that these halides, too, might react with the piperidine salt of N-pentamethylenedithiocarbamic acid similarly to the triarylmethyl halides. It was found that piperidine hydriodide was precipitated almost immediately upon the addition of diphenylarsyl iodide, dissolved in benzene, to the piperidine salt of the dithiocarbamic acid. A colorless, crystalline compound was isolated from the benzene solution which, according to the results obtained from an analysis and molecular weight determination, was N-pentamethylene-S-diphenylarsyldithiourethan.



Di- α -naphthylarsyl iodide, biphenylenearsyl iodide, 6-iodophenoxarsine, diphenylstibyl iodide and di-*p*-tolylstibyl iodide reacted with the piperidine salt in a manner entirely analogous to that described.

In the event that N-pentamethylene-S-diphenylarsyldithiourethan behaved similarly to the triarylmethyl analogs it should yield spontaneously, in solution, diphenylarsyl which would then polymerize, partly or com-

¹ Blicke, *J. Am. Chem. Soc.*, **45**, 544 (1923).

pletely, to tetraphenyldiarsyl. This compound, as well as other tetra-aryldiarsyls, absorbs with great rapidity an amount of oxygen which corresponds to that required for the formation of a peroxide.² Tetraphenyl-distibyl reacts with oxygen in a similar manner.³

In one series of experiments the reactivity of the dithiourethans toward oxygen was tested by the use of the original reaction mixture. A number of sealed tubes were prepared; each tube contained the iodide, the required amount of the piperidine salt of N-pentamethylenedithiocarbamic acid and bromobenzene. After twenty-four hours the tubes were broken in an absorption apparatus and the contents exposed to oxygen, with continuous agitation, for two hours. No absorption of oxygen was noticed in any instance. Absorption experiments were repeated with the isolated dithiourethans with negative results.

Phenyldichloro- and phenyldi-iodoarsine react readily with two molecular equivalents of the piperidine salt of the dithiocarbamic acid from phenylarsylene N-pentamethylenedithiocarbamate, $C_6H_5As[S-C(=S)-NC_5H_{10}]_2$. Other alkyl- and aryldihaloarsines would, undoubtedly, react in an analogous manner. Many alkyl- and aryldihaloarsines are liquids or low melting solids, hence, it is difficult if not impossible to identify small amounts of these substances. No entirely satisfactory derivatives have been described hitherto which can be used for identification purposes; the dithiocarbamate, however, which can be obtained in sufficient amount, from one drop of either of the above mentioned halides, seems to be especially suitable for this purpose because of the ease of its preparation,⁴ the high molecular weight, sharp melting point and the low loss of material on recrystallization.

Experimental Part

N-Pentamethylene-S-diphenylarsyldithiourethan.—Two hundredths of a mole of diphenylarsyl iodide, dissolved in the smallest possible amount of warm benzene, was added to 0.02 mole of the piperidine salt of *n*-pentamethylenedithiocarbamic acid,⁵ dissolved in warm benzene. Piperidine hydriodide precipitated immediately. The mixture was protected from moisture and after twelve hours the piperidine salt was removed by filtration and about 30 cc. of petroleum ether (30–60°) was added to the filtrate in order to precipitate a small quantity of piperidine hydriodide which had remained in solution. The hydriodide weighed 4.0 g.; the calculated amount is 4.2 g. To the benzene-petroleum ether solution there was added 150 cc. of petroleum ether whereupon the N-pentamethylene compound precipitated in crystalline form. The yield of the

² Blicke and Smith, *J. Am. Chem. Soc.*, **51**, 2272 (1929); Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 780 (1930).

³ Blicke and Oakdale, *ibid.*, **53**, 1025 (1931).

⁴ In order to obtain the reagent it is merely necessary to add piperidine to a solution of carbon disulfide in absolute ether; the piperidine salt of the dithiourethan precipitates immediately.

⁵ Cahours, *Ann. chim. phys.*, [3] **38**, 88 (1853); Ladenburg and Roth, *Ber.*, **17**, 514 (1884).

latter was 5.2 g. It was washed thoroughly with water to remove traces of piperidine hydriodide, dried and recrystallized from acetic acid or ethyl acetate.

Neither the original reaction mixture⁸ nor the pure, isolated dithiourethan absorbed oxygen.

The molecular weight was determined in boiling benzene by the Menzies method. Calcd. mol. wt., 389; found, 386.

Dissolved in acetone the compound decolorized potassium permanganate, as well as iodine, instantly.

Diphenylchloroarsine was formed when the benzene solution of the compound was treated with hydrogen chloride at ordinary temperature.

A few drops of sulfuric acid were added to an acetic acid solution of the material and the mixture boiled for a few minutes. Diphenylarsinic acid was obtained as a reaction product.

Di- α -naphthylarsyl iodide, biphenylenarsyl iodide, 6-iodophenoxarsine, diphenylstibyl iodide and di-*p*-tolylstibyl iodide reacted in a similar manner with the piperidine salt of the dithiocarbamic acid.

TABLE I
DITHIOURETHANS

Iodide used in preparation	M. p., °C.	Formulas	As, or Sb %		S, %	
			Calcd.	Found	Calcd.	Found
Diphenylarsyl	114–115	C ₁₈ H ₂₀ S ₂ NAs	19.26	19.42	16.47	16.61
Di- α -naphthylarsyl ^a	214–215	C ₂₆ H ₂₄ S ₂ NAs	15.33	14.99	13.11	12.57
Biphenylenarsyl ^b	155–158	C ₁₈ H ₁₈ S ₂ NAs	19.36	19.31	16.56	16.39
6-Iodophenoxarsine ^b	105–106	C ₁₃ H ₁₃ OS ₂ NAs	18.59	18.50	15.90	15.51
Diphenylstibyl ^c	124–127	C ₁₈ H ₂₀ S ₂ NSb	27.92	27.77	14.70	14.54
Di- <i>p</i> -tolylstibyl ^d	123–124	C ₂₀ H ₂₄ S ₂ NSb	26.23	26.19	13.82	13.66

^a Blicke and Smith, *J. Am. Chem. Soc.*, **51**, 1565 (1929).

^b Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 781 (1930).

^c Blicke, Oakdale and Smith, *ibid.*, **53**, 1026 (1931).

^d The preparation of this iodide will be described in a later paper.

Phenylarsylene N-Pentamethylenedithiocarbamate, C₆H₅As[S—C(=S)—NC₅H₁₀]₂.—The following experiment illustrates the serviceability of the piperidine salt of the dithiocarbamic acid as a reagent for the identification of a very small quantity of phenyldi-iodoarsine. To one drop (0.0306 g.) of the latter compound there was added 0.127 g. (five times the calcd. amount), of the piperidine salt dissolved in about 3 cc. of dry benzene. The mixture was protected from moisture and after twelve hours the benzene was allowed to evaporate. The crystalline residue was washed with water until the piperidine hydriodide and excess piperidine salt of the dithiocarbamic acid had

⁸ As a control experiment the reaction mixture obtained from 1.61 g. (0.005 mole) of triphenylmethyl bromide and 0.005 mole of the piperidine salt of the dithiocarbamic acid, dissolved in bromobenzene, was placed in the absorption apparatus and shaken vigorously. Previously, absorption experiments in the case of N-pentamethylene-S-triarylmethyldithiourethans had been carried out only with the isolated urethan. After one hour the reaction mixture had absorbed 60 cc. of oxygen and after two and one-half hours over 100 cc. had been absorbed. An absorption in excess of 56 cc., the required amount of gas for peroxide formation, is to be expected because of the union of the sulfur radical, formed during the dissociation of the dithiourethan, with oxygen. The formation of sulfur dioxide, or other volatile product, during the absorption naturally render the absorption procedure only a semi-quantitative one. Two-tenths of a gram of pure triphenylmethyl peroxide was isolated from the mixture.

been removed completely. The crude product weighed 0.022 g. One-half of the material was recrystallized from ethyl acetate; m. p. 173–174°.

Phenyldichloroarsine reacts in an analogous manner.

Anal. Calcd. for $C_{13}H_{25}S_4N_2As$: As, 15.87; S, 27.15. Found: As, 15.76; S, 26.92.

Summary

Diarylarsyl and diarylstibyl iodides react readily with the piperidine salt of N-pentamethylenedithiocarbamic acid to form N-pentamethylene-S-diarylarsyl- and N-pentamethylene-S-diarylstibylldithiourethans. Unlike the triarylmethyl analogs these substances do not undergo spontaneous decomposition in solution to form compounds of the type $R_2As-AsR_2$ and $R_2Sb-SbR_2$. Phenyldihaloarsines and the piperidine salt of the dithiourethan interact to yield a dithiocarbamate. Because of the advantageous properties of this substance the piperidine salt of the dithiocarbamic acid is suggested as a reagent for the identification of small quantities of alkyl- and aryldihaloarsines.

